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(21)Application number : 2000-321200 (71)Applicant : SANYO ELECTRIC CO LTD

(22)Date of filing : 20.10.2000 (72)Inventor : IKEDA HIROAKI

DOMOTO YOICHI

YAGI HIROMASA

TARUI HISAKI

FUJIMOTO MASAHISA

FUJITANI SHIN

SHIMA MASAKI

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(54) MANUFACTURING METHOD OF ELECTRODE FOR LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To manufacture an electrode for lithium secondary battery that has a high charge and discharge capacity and is excellent in charge and discharge cycle characteristics.

SOLUTION: The manufacturing method of lithium secondary battery comprises a method of forming a film by supplying the material from gas phase in which a film having an active material to be alloyed with lithium is formed on a current collector made of a metal which is not alloyed with lithium. A film is formed by a temperature under which a mixed layer dispersed with the components of the current collector is formed in the film at the vicinity of the surface interfacing with the current collector.

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## CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the electrode for lithium secondary batteries which is the manufacture approach of the electrode for lithium secondary batteries which forms the active material thin film which consists of a lithium and an active material to alloy using the approach of supplying a raw material from a gaseous phase and forming a thin film on the charge collector which consists of a lithium and a metal which is not alloyed, and is characterized by to form said active material thin film at the temperature by which the mixolimonion which said current-collection body constituent comes to be spread is formed in said active material thin film near the interface with said charge collector.

[Claim 2] The manufacture approach of the electrode for lithium secondary batteries according to claim 1 characterized by the formation temperature of said active material thin film being the temperature in which said active material and intermetallic compound of said current collection body constituent are not formed in said mixolimonion.

[Claim 3] The manufacture approach of the electrode for lithium secondary batteries according to claim 1 or 2 characterized by the formation temperature of said active material thin film being the temperature of less than 300 degrees C.

[Claim 4] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-3 characterized by performing heat treatment after

forming said active material thin film.

[Claim 5] The manufacture approach of the electrode for lithium secondary batteries according to claim 4 characterized by the temperature of said heat treatment being less than 650 degrees C.

[Claim 6] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-5 characterized by said active material using silicon or germanium as a principal component.

[Claim 7] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-6 characterized by said active material thin film being an amorphous silicon thin film or a microcrystal silicon thin film.

[Claim 8] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-6 to which said active material thin film is characterized by being an amorphous germanium thin film, a microcrystal germanium thin film, an amorphous silicon germanium alloy thin film, or a microcrystal silicon germanium alloy thin film.

[Claim 9] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-8 characterized by the thing of said charge collector for which the surface part is using copper as the principal component at least.

[Claim 10] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-9 characterized by the formation approach of said active material thin film being the sputtering method.

[Claim 11] The manufacture approach of the electrode for lithium secondary batteries given in any 1 term of claims 1-10 characterized by forming said active material thin film to said charge collector top intermittently.

[Claim 12] The manufacture approach of the electrode for lithium secondary batteries according to claim 11 characterized by forming said active material thin film on said charge collector intermittently by forming said active material thin film on said charge collector, installing said charge collector in the peripheral face of a drum-like electrode holder, and rotating this electrode holder.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of manufacturing the new electrode for lithium secondary batteries.

[0002]

[Description of the Prior Art] In recent years, cell properties, such as charge and discharge voltage, a charge-and-discharge cycle-life property, and a preservation property, are greatly influenced with the electrode with which the lithium secondary battery with which researches and developments are done briskly is used. Improvement in a cell property is achieved by improving from this the active material used for an electrode.

[0003] Although per weight and per volume could constitute the cell of a high energy density when the lithium metal was used as a negative-electrode active material, the lithium deposited in the shape of a dendrite at the time of charge, and there was a problem of causing an internal short circuit.

[0004] On the other hand, the lithium secondary battery using a lithium, the aluminum to alloy, silicon, tin, etc. as an electrode is electrochemically reported in the case of charge (SolidState Ionics, 113-115, p57 (1998)). The various rechargeable batteries which geometric capacity is large, and especially silicon has it as a negative electrode for cells in which a high capacity is shown, and make this a negative electrode are proposed among these (JP,10-255768,A). [ promising ] However, sufficient cycle property is not acquired from the alloy itself which is an electrode active material carrying out pulverization of this kind of alloy negative electrode by charge and discharge, and a current collection property getting worse.

[0005]

[Problem(s) to be Solved by the Invention] These people used silicon as the electrode

active material, and have proposed the electrode for lithium secondary batteries in which the microcrystal silicon thin film or the amorphous silicon thin film was formed on the charge collector, by the thin film formation approaches, such as a CVD method or the sputtering method, as an electrode for lithium secondary batteries in which a good charge-and-discharge cycle property is shown (Japanese Patent Application No. No. 301646 [ 11 to ] etc.).

[0006] The purpose of this invention is the electrode for lithium secondary batteries which used active material thin films, such as such a silicon thin film, and its charge-and-discharge capacity is high, and it is to offer the approach of manufacturing the electrode for lithium secondary batteries excellent in the charge-and-discharge cycle property.

[0007]

[Means for Solving the Problem] This invention is the manufacture approach of the electrode for lithium secondary batteries which forms the active material thin film which consists of a lithium and an active material to alloy using the approach of supplying a raw material from a gaseous phase and forming a thin film on the charge collector which consists of a lithium and a metal which is not alloyed, and is characterized by to form the above-mentioned thin film at the temperature by which the mixolimnion which a current-collection body constituent comes to spread is formed in the active material thin film near the interface with a charge collector.

[0008] As an approach of supplying a raw material from a gaseous phase and forming an active material thin film, the sputtering method, a CVD method, vacuum deposition, a spraying process, etc. are mentioned. The ingredients used as an active material in this invention are a lithium and an ingredient to alloy, for example, silicon, germanium, tin, lead, zinc, magnesium, sodium, aluminum, a gallium, an indium, etc. are mentioned.

[0009] From a viewpoint of being easy to form by the above-mentioned thin film formation approach as a thin film, the active material which uses silicon or germanium as a principal component is desirable. Moreover, especially the active material that uses silicon as a principal component from a viewpoint of a high charge-and-discharge capacity is desirable. Moreover, as for an active material thin film, it is desirable that they are an amorphous thin film or a microcrystal thin film. Therefore, as an active material thin film, an amorphous silicon thin film or a microcrystal silicon thin film is used preferably. An amorphous silicon thin film is a thin film with which about [ 520cm - ] one peak corresponding to a crystalline region is not detected substantially in Raman spectroscopic analysis, and a microcrystal silicon thin film is a thin film with which both about [ 520cm - ] one peak corresponding to a crystalline region and about

[ 480cm<sup>-1</sup> ] one peak corresponding to an amorphous field are detected substantially in Raman spectroscopic analysis. Moreover, an amorphous germanium thin film, a microcrystal germanium thin film, an amorphous silicon germanium alloy thin film, and a microcrystal silicon germanium alloy thin film can also be used preferably.

[0010] The charge collector used in this invention is formed from a lithium and the metal which is not alloyed. As a lithium and a metal which is not alloyed, copper etc. is mentioned, for example. In this invention, an active material thin film is formed at the temperature by which the mixolimnion which a current collection body constituent comes to spread is formed in the active material thin film near the interface of a charge collector and an active material thin film. That is, if the temperature at the time of forming an active material thin film (thin film formation temperature) becomes high, since it will become easy to diffuse a current collection body constituent in an active material thin film, in this invention, a current collection body constituent is fully spread, and an active material thin film is formed at the temperature by which the mixolimnion of a current collection body constituent and an active material component is fully formed in an active material thin film.

[0011] By spreading a current collection body constituent in an active material thin film, and forming a mixolimnion, the adhesion of a charge collector and an active material thin film becomes good. Moreover, since current collection body constituents are a lithium and a metal component which is not alloyed, when such a current collection body constituent is spread in an active material thin film, the expansion and contraction of an active material thin film at occlusion and the time of emitting become small relatively about a lithium. For this reason, since the stress accompanying expansion and contraction of an active material thin film becomes small near the interface with a charge collector, the exfoliation from the charge collector of the active material thin film by expansion and contraction of the volume can be prevented, and adhesion of a charge collector and an active material thin film can be made still better.

[0012] In such a mixolimnion, it turns out that the concentration is decreasing as the concentration of a current collection body constituent is [ / near the interface with a charge collector ] high and it goes to the front face of an active material thin film. Since the concentration is decreasing continuously in a mixolimnion, it is thought that the current collection body constituent in a mixolimnion forms an active material and the solid solution.

[0013] Moreover, if thin film formation temperature is raised, while a current collection body constituent will be superfluously spread in a thin film, the intermetallic compound of a current collection body constituent and an active material becomes is easy to be

formed. If such an intermetallic compound is formed, the sites which act as an active material will decrease in number about the active material atom used as a compound, and the charge-and-discharge capacity of an active material thin film will fall. Moreover, the adhesion of a charge collector and an active material thin film worsens by formation of an intermetallic compound. Therefore, it is desirable to form an active material thin film on a charge collector at the temperature in which an active material and the intermetallic compound of a current collection body constituent are not formed in a mixture. As such temperature, it is desirable that it is the temperature of less than 300 degrees C.

[0014] Moreover, in this invention, heat treatment may be performed, after forming an active material thin film. By performing such heat treatment, a current collection body constituent can be further diffused in a thin film. Therefore, when forming an active material thin film, and a current collection body constituent cannot fully be diffused in a thin film and the mixture of sufficient thickness is not able to be formed, it is desirable to perform such heat treatment. As for heat treatment, it is desirable to carry out by superfluous diffusion of a current collection body constituent as mentioned above on conditions in which the intermetallic compound of a current collection body constituent and an active material is not formed. As temperature of such heat treatment, it is 400 degrees C or less that it is the temperature of less than 650 degrees C desirable still more preferably.

[0015] In this invention, copper is desirable especially as a current collection body constituent diffused in an active material thin film. Since such copper is diffused in an active material thin film from the surface part of a charge collector, its thing of a charge collector for which the surface part is using copper as the principal component at least is desirable.

[0016] The power flux density supplied to the target containing the configuration atom of an active material in this invention when forming an active material thin film by the sputtering method is 50 W/cm<sup>2</sup>. It is desirable still more desirable that it is the following, and they are 6 W/cm<sup>2</sup>. It is the following. At this time, the injection of power may be performed using any of impression of DC electrical potential difference, RF electrical potential difference, or a pulse voltage.

[0017] Moreover, in this invention, it is desirable to form the active material thin film to a charge collector top intermittently. By forming an active material thin film intermittently, the temperature in the case of thin film formation, i.e., the maximum temperature which reaches in thin film formation, can be made low. Therefore, an active material thin film can be formed on the conditions in which the above intermetallic



compounds are hard to be formed. As an approach of forming a thin film intermittently, a charge collector is installed on the peripheral face of a drum-like electrode holder, and the method of making an active material thin film form on a charge collector is mentioned, rotating this electrode holder.

[0018] The desirable thin film formation conditions in the thin film formation approach which supplies a raw material from a gaseous phase and forms a thin film are explained below. As for substrate temperature, it is desirable that it is less than 300 degrees C as mentioned above. If substrate temperature becomes high too much, an active material and the intermetallic compound of a current collection body constituent may be formed.

[0019] As for a membrane formation rate, it is desirable that it is more than 0.01nm (0.1A/(second))/second. Since the effect of surface diffusion and a rearrangement will become remarkable and will become close to a thermal equilibrium process even if it is low temperature if a membrane formation rate becomes low too much, it becomes easy to produce an intermetallic compound.

[0020] The ambient pressure force (degree of vacuum) has desirable about 10-2-102Pa. If the ambient pressure force (degree of vacuum) becomes higher than this range, a thin film which deposited the powder-like particle may become is easy to be produced, and adhesion with a charge collector may worsen. Moreover, if the ambient pressure force (degree of vacuum) becomes lower than this range, a membrane formation rate will become extremely slow and it will become easy to produce an intermetallic compound as mentioned above.

[0021] The power flux density supplied to a target when forming an active material thin film by the sputtering method is 50 W/cm<sup>2</sup> as mentioned above. It is desirable still more desirable that it is the following, and they are 6 W/cm<sup>2</sup>. It is the following. If the power flux density supplied to a target becomes high too much, the effect of the radiant heat from the plasma will become large, and it will become easy to form an intermetallic compound.

[0022] Moreover, as sputtering gas, target ingredients, such as silicon, and the gas which does not react are desirable, and inert gas, such as helium, Ne, Ar, Kr, Xe, and Rn, is desirable from such a viewpoint. Also in these, it is easy to generate the plasma and especially Ar gas with the high effectiveness of sputtering is desirable.

[0023] Moreover, as a target used for sputtering, the target of a single crystal or polycrystal is desirable, and, as for purity, it is desirable that it is 99% or more. This is because mixing of the impurity to the active material thin film to form decreases.

[0024] Moreover, as a pressure in the chamber before starting thin film formation, it is desirable that it is 0.1Pa or less. This is also because mixing of the impurity to an active

material thin film can be lessened.

[0025] Before forming a thin film, it is desirable to pretreat a plasma exposure etc. to the charge collector which is a substrate. As a plasma exposure of such pretreatment, Ar plasma exposure, a hydrogen plasma exposure, etc. are mentioned. The front face of a charge collector can be defecated by performing such pretreatment. It is desirable to make it substrate temperature not become 300 degrees C or more by such pretreatment, since the temperature rise of a substrate is also produced.

[0026] Moreover, as for the charge collector which is a substrate, washing, before forming a thin film is desirable in order to defecate a front face. As a cleaning agent, what combined water, an organic solvent, an acid, alkali, neutral detergent, and these is used preferably.

[0027] When performing heat treatment after forming a thin film, as mentioned above, it is desirable still more desirable that it is less than 650 degrees C, and heat treatment temperature is 400 degrees C or less. If heat treatment temperature becomes high, an intermetallic compound will become is easy to be formed as mentioned above.

[0028] Moreover, it is desirable to perform intermittently formation of the active material thin film to a charge collector top. Therefore, it is desirable to install a charge collector on the peripheral face of a drum-like electrode holder as mentioned above, to make an active material thin film form on a charge collector, rotating an electrode holder, or to attach a charge collector on the reciprocating electrode holder, and to make an active material thin film form intermittently on a charge collector. Furthermore, an active material thin film can be intermittently formed by preparing two or more targets for forming an active material thin film, and being made to carry out sequential passage of the field where a charge collector counters a target. Thus, the temperature rise of a substrate can be controlled by forming an active material thin film intermittently. Moreover, as for the thickness of one thin film formation, it is desirable that it is 1 micrometer or less.

[0029]

[Embodiment of the Invention] It is possible to change this invention suitably in the range which is not limited to the following examples at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0030] (Experiment 1)

[Production of a negative electrode] As a charge collector, using the rolling copper foil (thickness of 26 micrometers) which carried out surface roughening of the front face, the parallel monotonous mold RF sputtering system was used, and the silicon thin film

was formed on this charge collector by depositing copper with an electrolytic decomposition process on a front face. As a target, 99.999% of silicon single crystal was used, using only Ar gas as a controlled atmosphere of sputtering. In the thin film formation conditions shown in Table 1 and 2, the negative electrode of examples 1-7 and the examples 1-3 of a comparison was produced, adjusting the opening of Ar quantity of gas flow or an exhaust air bulb. Thickness of a silicon thin film was set to about 6 micrometers.

[0031] In examples 1-3 and the examples 1-2 of a comparison, substrate temperature was changed, thin film formation temperature (the highest attainment temperature) was changed, and the silicon thin film (active material thin film) was formed. In the example 4 and the example 3 of a comparison, it heat-treated after thin film formation on the conditions shown in Table 2. Examples 5-7 changed the power flux density supplied to a target, and formed the thin film.

[0032] Raman spectroscopic analysis was performed about the formed silicon thin film, and the crystallinity was identified. What about [ 480cm<sup>-1</sup> ] one peak is substantially accepted, and about [ 520cm<sup>-1</sup> ] one peak is not substantially accepted in was taken as the "amorphous substance." Moreover, what about [ 480cm<sup>-1</sup> ] one peak is not substantially accepted, but only about [ 520cm<sup>-1</sup> ] one peak is substantially accepted in was used as "polycrystal."

[0033] In addition, the silicon thin film used the mask for the 2.5cmx2.5cm field on copper foil, and formed it in it restrictively. After forming an active material thin film, the negative-electrode tab was attached on the field of copper foil in which the silicon thin film is not formed, and the negative electrode was completed.

[0034] [production of a positive electrode] -- LiCoO<sub>2</sub> the powder 90 weight section and the artificial-graphite powder 5 weight section as electric conduction material -- the polytetrafluoroethylene as a binder -- N-methyl pyrrolidone water solution of 5 % of the weight of 5 weight \*\*\*\*\* -- mixing -- a positive electrode -- a mixture -- it considered as the slurry. With the doctor blade method, after applying this slurry on the 2cmx2cm field of the aluminium foil (thickness of 18 micrometers) which is a positive-electrode charge collector, it was dried, and the positive-active-material layer was formed. The positive-electrode tab was attached on the field of the aluminium foil which did not apply a positive-active-material layer, and the positive electrode was completed.

[0035] [Production of the electrolytic solution] It is LiPF<sub>6</sub> to the constant volume mixed solvent of ethylene carbonate and dimethyl carbonate. One mol /dissolved L, the electrolytic solution was prepared, and this was used in production of the following cells.

[0036] [Production of a cell] Drawing 2 is the perspective view showing the produced lithium secondary battery. Drawing 3 is the cross section showing the produced lithium secondary battery. As shown in drawing 3, the positive electrode and the negative electrode are inserted into the sheathing object 10 which consists of an aluminum laminate film. On the negative-electrode charge collector 11, the silicon thin film 12 as a negative-electrode active material is formed, and the positive-active-material layer 14 is formed on the positive-electrode charge collector 13. The silicon thin film 12 and the positive-active-material layer 14 are arranged so that it may counter through a separator 15. The above-mentioned electrolytic solution is poured in into the sheathing object 10. Joining obturates the edge of the sheathing object 10 and obturation section 10a is formed. The negative-electrode tab 17 attached in the negative-electrode charge collector 11 is taken out outside through this obturation section 10a. In addition, although not illustrated by drawing 3, the positive-electrode tab 18 attached in the positive-electrode charge collector 13 is similarly taken out outside through obturation section 10a.

[0037] [Charge-and-discharge cycle trial] The charge-and-discharge cycle trial was performed about the lithium secondary battery produced as mentioned above. After charging until the conditions of charge and discharge were set to charge termination capacity 9mAh by 9mA of charging currents, it discharged until it was set to discharge-final-voltage 2.75V by 9mA of discharge currents, and discharge capacity and charge-and-discharge effectiveness were searched for about each cell as charge and discharge of 1 cycle. [ in / for this / 1 cycle eye, 5 cycle eye, and 20 cycle eye ] A result is shown in Table 1 and 2. In addition, the unit sccm of the flow rate in the following tables is a volumetric flow rate (a part for cm<sup>3</sup>/) per for [ of 0 degree C and one atmospheric pressure (101.33kPa) ] 1 minute, and is standard cubic centimeters per minute. It is abbreviation.

[0038]

[Table 1]

[0039]

[Table 2]

[0040] If thin film formation temperature (the highest attainment temperature) is less than 300 degrees C so that clearly from the result of the examples 1-3 shown in Table 1,

and the examples 1-2 of a comparison, a high discharge capacity and good charge-and-discharge effectiveness are acquired.

[0041] It turns out that the crystallinity of a silicon thin film will become polycrystal if the temperature of heat treatment performed after thin film formation becomes 650 degrees C so that clearly from the result of the example 4 shown in the example 1 shown in Table 1, and Table 2, and the example 3 of a comparison, and discharge capacity and charge-and-discharge effectiveness fall. This shows that it is 400 degrees C or less that the temperature of heat treatment is less than 650 degrees C desirable still more preferably.

[0042] The power flux density supplied to the target in the case of thin film formation so that clearly [ the example 1 list shown in Table 1 ] from the result of the examples 5-7 shown in Table 2 is 4.94 W/cm<sup>2</sup>. In the following range, it turns out that a high discharge capacity and good charge-and-discharge effectiveness are acquired.

[0043] Next, substrate temperature was changed and concentration distribution of the copper element in the depth direction was measured by SIMS (secondary ion mass spectroscopy) about the negative electrode of the examples 1-3 which thin film formation temperature (the highest attainment temperature) was changed, and formed it, and the examples 1-2 of a comparison. As a negative electrode, the negative electrode before a charge and discharge test is used, and it is O<sub>2</sub>+. It uses for the source of sputtering and is a copper element (63Cu<sup>+</sup>). Concentration distribution was measured.

[0044] Drawing 4 - drawing 8 show concentration distribution of the copper of the depth direction of the negative electrode produced in examples 1-3 and the examples 1-2 of a comparison, an axis of abscissa shows the depth (micrometer), and the axis of ordinate shows the atomic consistency (atoms/cc:atoms/cm<sup>3</sup>). In an example 2 and drawing 6 , an example 3 and drawing 7 show the example 1 of a comparison, and, as for drawing 4 , drawing 8 shows [ an example 1 and drawing 5 ] the example 2 of a comparison, respectively.

[0045] Also in any of drawing 4 - drawing 8 , [ near the front face ], copper concentration is almost uniform and the low field exists relatively. Moreover, the field which copper concentration is increasing exists as it tends toward an interface with a charge collector from the front face of an active material thin film. Since the field which such copper concentration increases exists, it turns out that the mixing zone of an active material thin film and a copper element exists by diffusion of the copper element from a charge collector [ near the interface of an active material thin film and a charge collector ]. It is thought that the high adhesion between a charge collector and an active material thin film is acquired by such existence of a mixing zone (mixolimnion).

[0046] In the examples 1-3 ( drawing 4 - drawing 6 ) formed on the conditions that substrate temperature is comparatively low, the copper concentration near the active material thin film front face is 1020 atoms/cc (atoms/cm<sup>3</sup>) (about 1%). On the other hand, in the examples 1-2 ( drawing 7 - drawing 8 ) of a comparison which formed the active material thin film at comparatively high substrate temperature, the copper concentration near the active material thin film front face has become more than 1021 atoms/cc (atoms/cm<sup>3</sup>) (about 10%). If an active material thin film is formed at higher substrate temperature from these things, in order that copper may be spread in the whole active material thin film and the concentration of an active material may decrease relatively, it is thought that discharge capacity falls. Moreover, when copper exists by high concentration in an active material thin film, it is thought that a cycle property falls. This is considered to be for an intermetallic compound to generate in an active material thin film probably.

[0047] (Experiment 2)

[Production of a negative electrode] The silicon thin film was formed using the sputtering system which has a rotation electrode holder as shown in drawing 1 as an RF sputtering system. As a charge collector, the silicon thin film was formed on it using what was used for the experiment 1, and the same thing. Installing a charge collector on the peripheral face of the rotation electrode holder 1 shown in drawing 1 , and rotating the rotation electrode holder 1, supplied RF (RF) power to the target 2 from RF generator 3, it was made to generate the Ar plasma 4, and the silicon thin film was formed on the charge collector. Rotational speed of the rotation electrode holder 1 was set to about 10 rpm, and other thin film formation conditions were carried out as shown in Table 3. In addition, the same thing as experiment 1 was used for the target, using only Ar gas as sputtering gas. The thickness of a silicon thin film was formed so that it might be set to about 6 micrometers.

[0048] [Production of a cell and charge-and-discharge cycle trial] Using the same positive electrode as experiment 1, the lithium secondary battery was produced like the experiment 1, and the charge-and-discharge cycle trial as well as experiment 1 was performed. A result is shown in Table 3.

[0049]

[Table 3]

[0050] In an example 8, other formation conditions are the same compared with an example 1, and although the power flux density supplied to a target is large a little, thin film formation temperature (the highest attainment temperature) is lower than an example 1, so that clearly from the result shown in Table 3. Since this forms the active material thin film, installing a charge collector on a rotation electrode holder, and rotating a rotation electrode holder, formation of the silicon thin film to a charge collector top is performed intermittently, and it is considered that the highest attainment temperature is controlled low for this reason. Moreover, it turns out that discharge capacity and charge-and-discharge effectiveness are fitness a little compared with an example 1.

[0051] (Experiment 3) Using the same parallel monotonous mold sputtering system as experiment 1, the power supplied to a target was replaced with RF (RF) power, and was made into DC power or pulse power, except considering as the power flux density shown in Table 4, the silicon thin film was formed on the charge collector like the example 1 of experiment 1, and the negative electrode was produced like the experiment 1.

[0052] [Production of a cell and charge-and-discharge cycle trial] Using the same positive electrode as experiment 1, the lithium secondary battery was produced like the experiment 1, and the charge-and-discharge cycle trial as well as experiment 1 was



performed. A result is shown in Table 4.

[0053]

[Table 4]

[0054] By replacing with an RF generator and using a DC power supply or a pulse power source shows that thin film formation temperature (the highest attainment temperature) is low compared with an example 1 so that clearly from the result shown in Table 4. Moreover, the good result as an example 1 with almost same discharge capacity and charge-and-discharge effectiveness of a lithium secondary battery which were acquired is obtained.

[0055] In the above-mentioned example, although the active material thin film is formed by the sputtering method, this invention is not limited to this and may use other thin film formation approaches, such as a CVD method.

[0056]

[Effect of the Invention] According to this invention, it is high, and charge-and-discharge capacity is stabilized and can manufacture the electrode for lithium secondary batteries excellent in the charge-and-discharge cycle property.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] The typical block diagram showing the sputtering system which has the rotation electrode holder used in the example according to this invention.

[Drawing 2] The perspective view showing the lithium secondary battery produced in the example according to this invention.

[Drawing 3] The cross section showing the lithium secondary battery produced in the example according to this invention.

[Drawing 4] Drawing showing concentration distribution of the copper element of the depth direction in the electrode of an example 1.

[Drawing 5] Drawing showing concentration distribution of the copper element of the depth direction in the electrode of an example 2.

[Drawing 6] Drawing showing concentration distribution of the copper element of the depth direction in the electrode of an example 3.

[Drawing 7] Drawing showing concentration distribution of the copper element of the depth direction in the electrode of the example 1 of a comparison.

[Drawing 8] Drawing showing concentration distribution of the copper element of the depth direction in the electrode of the example 2 of a comparison.

### [Description of Notations]

1 -- Rotation electrode holder

2 -- Target

3 -- RF generator

4 -- Ar plasma

- 10 -- Sheathing object
- 11 -- Negative-electrode charge collector
- 12 -- Silicon thin film
- 13 -- Positive-electrode charge collector
- 14 -- Positive-active-material layer
- 15 -- Separator
- 16 -- Electrolytic solution
- 17 -- Negative-electrode tab
- 18 -- Positive-electrode tab